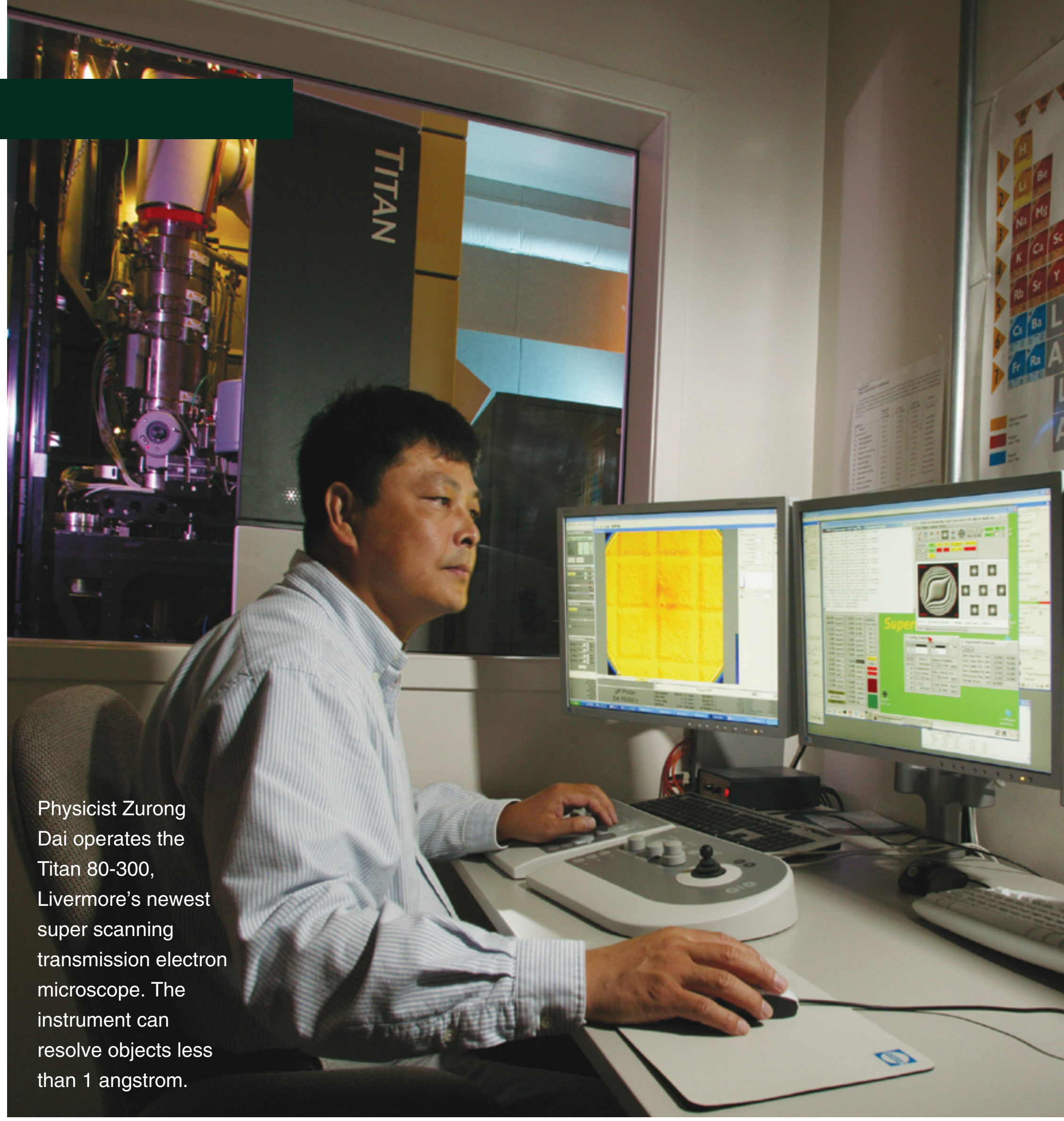
Imaging at the Atomic Level



Physicist Zurong Dai operates the Titan 80-300, Livermore's newest super scanning transmission electron microscope. The instrument can resolve objects less than 1 angstrom.

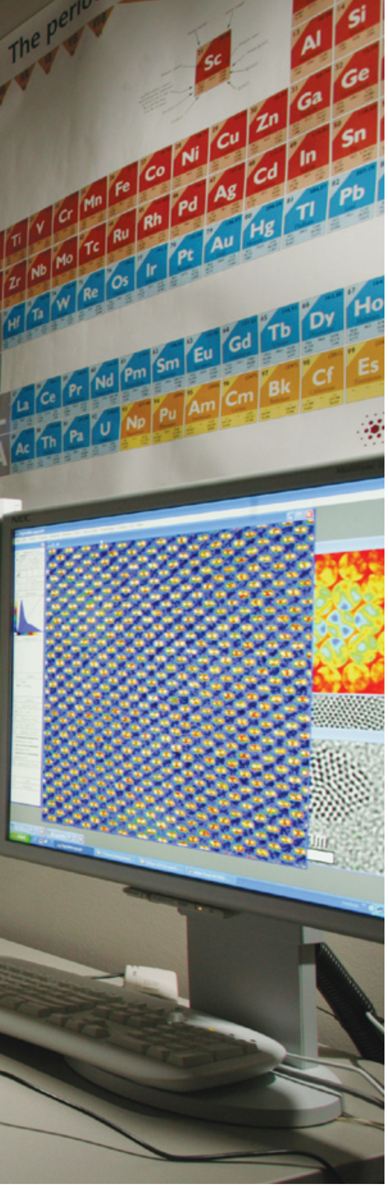
FOLLOWING the successful recovery of the National Aeronautics and Space Administration's (NASA's) Stardust sample-return capsule in January 2006, scientists began extracting and analyzing samples from Comet Wild 2 that were embedded in the spacecraft's cometary particle collector. Particles were trapped both in the collector's silica aerogel cells and in craters that formed in the aluminum foil wrapped around the collector grid walls. In December 2006, Livermore scientists were among the researchers who announced results of some of the first cometary particle analyses. (See *S&TR,* April 2007, pp. 4–11.) Those analyses were greatly aided by the Laboratory's super scanning transmission electron microscope known as SuperSTEM—the highest resolution microscope in the world.

"Stardust particles are aggregates of carbonaceous matter, glass, and crystals with a grain size of 2 to 5 nanometers," says physicist John Bradley, director of Livermore's branch of the University of California's Institute of Geophysics and Planetary Physics. "Understanding such complex assemblages requires mapping them with the highest possible spatial resolution because a portion of the most significant information is detectable only on the atomic scale."

SuperSTEM technology uses monochromators and image correctors for analyzing a particle's composition on the atomic scale, resulting in stunning pictures magnified more than l million times. Using SuperSTEM and other analytical instruments, many of them located at Livermore, scientists have found Comet Wild 2 is full of complex minerals and other material that originated in the inner solar system. Yet, the comet was formed a long distance from the Sun, far beyond the orbit of Neptune.

SuperSTEM is an advanced form of a transmission electron microscope, which evolved from the first electron microscope developed in Germany in 1931. A transmission electron microscope uses a focused beam of energetic electrons to penetrate an extremely thin-sliced specimen. The instrument allows researchers to analyze the shape and size of particles making up a specimen, its constituent elements and compounds, and the arrangement of the atoms in the specimen's crystalline lattice.

SuperSTEM focuses an electron beam on a narrow area of the sample and then scans it in a raster pattern. The rastering of the electron beam makes possible analysis techniques such as electron



energy-loss spectroscopy (EELS), which provides information on the electronic properties of materials. EELS can derive the identity and chemical and electronic states of atoms by measuring the amount of energy lost in interactions with electrons from SuperSTEM's beam. This information is obtained simultaneously as an image builds up, thereby forming a direct correlation between the image and electronic data.

Record Resolution

Bradley focused on emerging SuperSTEM technology in 1999 with the goal of achieving a resolution of less than 1 angstrom (0.1 nanometer) to address challenges in astromaterials science. "We had never achieved subangstrom resolution, but I knew we could effectively use this technology to examine fine-grained extraterrestrial materials from Stardust and other space missions," says Bradley. (Atoms range in diameter between 1 and 3 angstroms; the space between atoms in a crystalline lattice is about 4 angstroms.)

Bradley met with microscope experts from the FEI Company in Eindhoven, Netherlands, to discuss the essential elements of a SuperSTEM. The goal was to image structures with atomic resolution and simultaneously provide information on the chemical composition, bonding, and electronic structure of the material under analysis. SuperSTEM's monochromator would reduce energy spread in the electron probe from about 1 to 0.1 electronvolt—a capability comparable to that provided by synchrotron facilities. In addition, spherical aberration correctors would remove image blurring in the lens of the microscope to improve image resolution by nearly tenfold.

The use of both aberration correctors and monochromators, not previously combined in transmission electron microscopes, would mean tighter, brighter beams yielding a stronger signal, higher imaging contrast, greater analytical sensitivity, and unprecedented spatial and spectral resolution. The specifications also included digital imaging, an ultrahigh-stability power supply, and systems to suppress mechanical vibration and electronic noise.

The first machine produced by FEI, called Tecnai, was funded jointly by NASA's Sample Return Laboratory Instrument and Data Analysis Program and Lawrence Livermore. Tecnai was installed at Livermore in 2004 in a laboratory designed specifically to dampen vibrations, suppress ambient magnetic fields, and reduce variations in temperature. "The instrument is so sensitive that I have to hold my breath when taking a picture to keep the image from blurring," says Livermore physicist Zurong Dai.

Tecnai, which can achieve about 1.4-angstrom resolution, incorporates some but not all of the SuperSTEM features Bradley requested. Its most important feature is a monochromator that operates at 200 kiloelectronvolts. The monochromator, located at the beam source, reduces energy spread in the beam for high-resolution EELS to reveal bonding, valence state, and electronic properties. Tecnai's energy resolution (0.1 electronvolt) provides more than 100 times improved spatial resolution.

Livermore scientists and colleagues from other research institutions have used Tecnai to study the mineralogical and chemical composition of Stardust samples. Materials scientists and biologists have also found the machine's extreme powers of magnification to be invaluable.

Miaofang Chi, a University of California at Davis student and a participant in Livermore's Student Employee Graduate Research Fellowship Program, used EELS on Tecnai to identify osbornite (titanium nitride), a mineral formed at high temperatures that was found imbedded in Stardust silicates. "The machine is easy to operate and user friendly," she says. "Everything is computerized. For example, the microscope alignment can be stored and easily reloaded for another experiment."

Chi has applied her expertise gained from the Stardust project to study man-made compounds called vanadium perovskites. These compounds have strong electron correlations with physical properties that can be tailored by substituting different elements. Some of them are candidates for multiferroic materials, which exhibit both magnetic and ferroelectric properties.

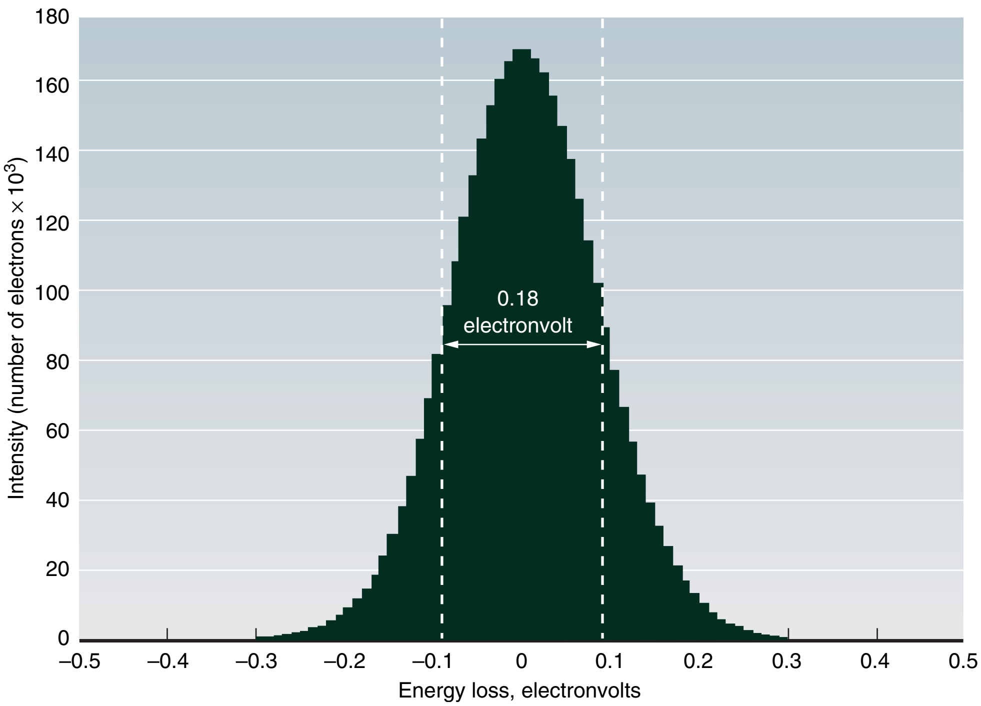
Vanadium perovskites are useful for semiconductor devices, switches, and data storage. Working with chemist Nigel Browning of the Chemistry, Materials, Earth, and Life Sciences Directorate, Chi is examining the electronic and atomic structures of perovskite thin films and nanomaterials. In addition to improving understanding of electron correlated materials, this work could lead to entirely new materials.

Titan More Advanced

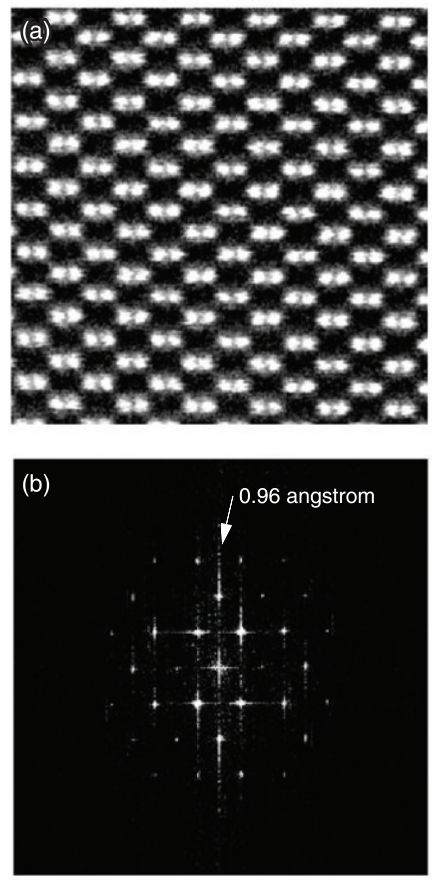
Tecnai is being replaced with a more advanced SuperSTEM called Titan 80-300. This machine features the same monochromator as Tecnai but has two additional spherical aberration correctors to resolve features as small as 0.8 angstrom. Spherical aberrations have long interfered with the ability to clearly image material interfaces with atomic detail.

Titan operators will be able to choose voltages accelerating between 80 and 300 kiloelectronvolts. A higher voltage improves spatial resolution and permits thicker samples to be examined. However, some specimens can be sensitive to damage by high-energy electrons. In such instances, operators will be able to choose a lower setting.

Titan will be used in Livermore's continuing Stardust particle analysis effort and in an increasing number of materials science–related research projects, especially those involving novel nanomaterials. Bradley explains that in nanomaterials, the atomic structure of layer interfaces and the thickness of extremely thin



Titan's monochromator reduces energy spread in the beam used for high-resolution electron energy-loss spectroscopy, which yields information on the electronic properties of materials. This graph shows that Titan achieves an average 0.18-electronvolt energy resolution when operating at 300 kiloelectronvolts. In contrast, other 300-kiloelectronvolt scanning transmission electron microscopes typically obtain about 0.75-electronvolt resolution under ideal conditions.



(a) Titan's resolving power of less than 1 angstrom is shown here with silicon "dumbbells." (b) A corresponding diffraction pattern of the same sample indicates that a subangstrom spatial resolution was achieved.

layers, many measuring less than 1 nanometer, determine their properties. Therefore, images with ultrahigh atomic resolution are needed to understand a material's properties and dimensions and to improve its performance. Chi, for example, plans to use Titan to study the effects of oxygen vacancies within atomic lattices on nanomaterials used in electronic switches and fuel cells.

Bradley notes that SuperSTEM is one of several advanced analytical instruments at Livermore. Other machines include the nanometer-scale secondary-ion mass spectrometer known as NanoSIMS, a dual-beam focused ion beam, an ultramicrotome (for cutting cell sections), and a clean room.

By combining microanalytic instruments such as these, Livermore researchers are at the forefront of characterization materials at the nanoscale. Bradley says, "We are developing an integrated microanalysis capability to enable a new level of investigations into the mineralogical, chemical, and isotopic properties of nanomaterials. The initial development is being carried out on natural nanomaterials captured during the Stardust mission. The Stardust studies are developing capabilities directly applicable to Laboratory missions in stockpile stewardship and homeland security that require characterization on the nanoscale and beyond."

For example, researchers plan to use Titan to determine the microstructure of natural uranium minerals as references for nuclear forensics investigations. Other applications include studying grain boundaries in semiconductors and determining the composition of room-temperature gamma-ray detectors.

The National Center for Electron Microscopy at Lawrence Berkeley National Laboratory has also purchased a Titan 80-300. "Over the next few years, I expect that many institutions will be acquiring a similar machine," says Bradley. As word spreads about SuperSTEM's capabilities, Livermore researchers in disciplines ranging from biological science to semiconductors are planning to use it as a powerful tool for imaging and analysis. Their results should allow them to better understand existing materials and to develop new materials with novel characteristics.

—Arnie Heller

Key Words: electron microscope, electron energy-loss spectroscopy (EELS), monochromator, nanomaterials, Stardust spacecraft, super scanning transmission electron microscope (SuperSTEM).

For further information contact John Bradley (925) 423-0666 (bradley33@llnl.gov).